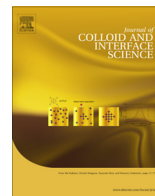




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The use of preformed nanoparticles in the production of heterogeneous catalysts

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ABSTRACT

Preformed iron oxide nanoparticles have been successfully assembled onto alumina and MCM-41 support materials. The particles are found to disperse evenly over the surface of the silicate; however, in the case of the alumina we find that in addition to areas of even distribution there is also some clustering of the particles. The materials are stable under heat treatment, with no signs of further aggregation during calcination. We investigate the reducibility of the materials through H₂-TPR studies and we find that the particles are reducible around 500–550 °C. The reduction process is complete at temperatures where MCM-41 can undergo degradation, supporting that the alumina based materials are more suited to the multiple base oxidation reduction steps in the catalytic cycle.

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1. Introduction

The use of nanoparticles as Fischer–Tropsch (FT) catalysts has attracted increasing interest in recent times [1–3]. This has largely arisen out of their size dependent properties, ease of preparation for FT active metals and large number of atoms at their surface. Despite the development in a number of chemical approaches [4] that give control over particle size and composition, and the subsequent assemblage of these preformed particles onto supports [5], very few literature examples involving the addition of preformed nanoparticles to support materials exist [3,6,7]. This method is highly advantageous as it allows greater control over what species are assembled onto a support material and it removes the dispersion problems seen with metal clusters in traditional FT catalysts [8]. Further research is required to develop new systems based on the assemblage of preformed particles onto supports so that an assessment of the benefits of these materials can be made. This work involves the development of such new systems.

One of the main advantages offered by using preformed nanoparticles over those formed in situ using co-precipitation and sol–gel is the ability to easily access the size dependent properties of the catalyst for the generation of particular alkanes. Producing narrow range of particle sizes for FT containing metals is easily

achieved using hydrothermal high temperature reactions [9,10]. Co-precipitation and sol–gel methods that are used in industrial processes result in particles that tend to be less homogeneous in both size and composition [11]. Often these materials also have stability issues arising from the leaching of the deposited metal species at the elevated temperatures required for metal reduction [12]. Some balance needs to be achieved between the simple precursors, scale and simple purification techniques offered by co-precipitation and sol–gel with the structural control and stability seen in the preformed nanoparticles systems.

FT active metals generally involve iron, cobalt, nickel and ruthenium due to the preference in production of diesel fuel and linear, high molecular weight alkanes. Cobalt catalysts are the most developed FT catalyst as syngas is normally derived from natural gas, which has a higher hydrogen/carbon monoxide ratio and relatively low sulfur content. Although there have been relatively few reports of the use of preformed Co nanoparticles, many examples exist on size effects for relatively monodisperse Co containing nanoparticles [13–17]. Despite our own work [5,7], few iron based preformed particle systems have been explored. Iron based catalysts are preferred for low grade feedstocks based on coal. Synthesis gas in this case has a higher sulfur content and a low H₂/CO ratio due to their higher water–gas-shift activity. Iron is advantageous, due to its relatively low costs and higher FT activity. Furthermore, the synthesis of iron based systems via hydrothermal methods is well established in the literature [4,18,19] and preformed particles have been shown to be readily incorporated into Mobil Composition of Matter (MCM) materials during their synthe-

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sis [20]. Iron based nanoparticles are advantageous over their cobalt counterparts as not only are their syntheses more developed for commercialization, but also because they offer a more accessible range of bimetallic systems. With the exception of cobalt ferrite [21], complexities tend to arise in cobalt nanoparticle synthesis because cobalt possesses multiple crystal structures that are close in energy. Hence subtle changes in temperature or surfactant lead to much more dramatic effects in surface chemistry, resultant size and shape of nanoparticles formed in comparison to iron [22]. Based on this we have explored the ability to assemble preformed iron oxide particles onto supports.

In this paper we examine the assemblage of preformed iron oxide nanoparticles, onto two support materials, a mesoporous silica, MCM-41, and an alumina, puralox SBa200. These materials are ideal candidates for use as high temperature FT catalysts. We use a variety of characterization techniques to evaluate the assemblage of the preformed particles onto supports, determining if this methodology is accessible for other nanoparticles and supports or is limited to the previously studied FePt and MCM silicas.

2. Materials and methods

2.1. Synthesis of iron oxide nanoparticles

Iron oxide nanoparticles were synthesized using the hydrothermal technique [18] involving the addition of $\text{Fe}(\text{CO})_5$ (0.2 mL, 1.52 mmol, Strem Chemicals Inc.) to a 10 mL solution of octyl ether (Sigma Aldrich) with oleic acid (1.92 mL, 6.08 mmol Sigma-Aldrich) at 100 °C. Following the rapid injection of the iron precursor the solution was heated to reflux at a rate of 10 degree/min. After 1 h the reaction was cooled to room temperature where 0.34 g of anhydrous $(\text{CH}_3)_3\text{NO}$ (Sigma-Aldrich) was added and the solution heated to 130 °C. After being maintained at this temperature for 2 h the solution was returned to reflux and left for an additional hour. The solution was then cooled to room temperature and the particles purified by centrifugation with ethanol.

2.2. Assemblage of nanoparticles onto support materials

The particles were subsequently reacted with either a well ordered silicate (MCM-41), that had been prepared via a literature preparation [23] and then calcined at 550 °C for 1 h in N_2 and overnight in air (pore diameter ca. 27 Å BET 1030 m^2/g), or a commercially available alumina (SASOL puralox SBa200) that had been calcined for 2.5 h at 750 °C (pore diameter ca. 84 Å BET 161 m^2/g). The samples will be referred to Fe-MCM and Fe-puralox respectively. A typical procedure involved the addition of approximately 200 mg of nanoparticles suspended in 10 mL hexane to a solution of 2 g of support material in 20 mL hexane overnight. The process was deemed complete when the hexane became colorless. The pale brown/red powder (~2.17 g) was washed with more hexane and collected via filtration and dried under vacuum. Temperature stability of the catalysts was explored by calcination under two different thermal conditions. Temperatures of 200 °C and 550 °C were used, for a total of four hours. In each, the first hour was under a flow of nitrogen with a further three hours under a flow of air.

2.3. Characterization

Transmission electron microscopy (TEM) was conducted on three microscopes; a JEOL 3000F operating at 300 kV and equipped with a Gatan Orius SC1000, an FEI Tecnai F20 operating at 200 kV and equipped with a Gatan Orius SC600 camera, and an FEI CM200 operating at 197 kV equipped with a Gatan GIF200. Compositional analysis in the TEM was performed using energy dispersive X-ray

(EDX) spectroscopy (Oxford Instruments, JEOL 3000F and FEI Tecnai F20) and energy filtered TEM (EFTEM) (Gatan, CM200).

Powder X-ray diffraction (XRD) patterns were recorded at room temperature on a Siemens D5000 diffractometer with $\text{Cu K}\alpha$ radiation generated at 40 kV and 35 mA. The amount of Fe, Al and Si in the calcined catalysts was determined by X-ray Fluorescence (XRF) Spectrometry (Ultra Trace Pty Ltd.). Samples were cast using a 12:22 flux to form a glass bead that could be analyzed by XRF.

N_2 absorption and desorption isotherms were measured at 77 K for both the calcined support materials and calcined catalysts using a TriStar II 3020. Prior to measurement the sample (~0.1 g) was degassed under vacuum overnight at 130 °C. Specific surface areas were estimated using BET analysis and pore diameters by BJH desorption.

Thermal gravimetric analysis (TGA) was performed on the samples using a TA SDT Q600. The sample was initially dried at 105 °C for 10 min under a flow (50 mL/min) of air. After cooling to ambient temperature measurements were carried out with a linear ramp to 1000 °C at 10 °C/min with a flow of 8% H_2 in N_2 (50 mL/min).

The reductive behavior of the iron oxide supported catalysts was studied using a Micromeritics AutoChem II 2920 apparatus. Around 30 mg of calcined sample was initially flushed with Ar at 200 °C for half an hour. Subsequently the sample was cooled to ambient temperature and the gas was then switched to 8% H_2 in N_2 and the temperature increased up to 900 °C. A downstream ice/salt trap was used to ensure any water produced was retained. The thermal conductivity detector (TCD) used to monitor the rate of H_2 consumption was calibrated prior to use using the reduction of AgO as a reference.

3. Results and discussion

The iron oxide particles synthesized were shown by TEM analysis (Supplementary Material Fig. S1) to consist of crystalline particles with a range of sizes 2–10 nm. The methodology used [18] is intended to produce nanocrystals of $\gamma\text{-Fe}_2\text{O}_3$, we find that our selected area electron diffraction (SAED) and XRD spacings (Supplementary Material Fig. S2 and Table S1) support particles being either $\gamma\text{-Fe}_2\text{O}_3$ or Fe_3O_4 structure.

Two support materials have been investigated in this assemblage study. The materials have significant differences not only in chemical composition, but also in surface area and pore structures. The MCM-41 silicate used in this study has been characterized and discussed previously [7,24,25] and is comprised of a well ordered porous system. The alumina alternative, Puralox SBa200, was supplied by SASOL. TEM imaging of Puralox SBa200 found the material consists of smaller crystals (~20 nm) that aggregate into larger clusters ~200–1000 nm in diameter. SAED and XRD (Supplementary Material Fig. S3) confirmed the $\gamma\text{-Al}_2\text{O}_3$ structure, with the predominant d-spacings measured. To ensure the support was fully dehydrated before assemblage of the particles, the support was calcined in air at 750 °C. Using BET surface area measurements (Supplementary Material Table S2) we found that 2.5 h calcination results in a slight decrease in surface area (185 to 162 m^2/g) but an increase in the pore diameter (75 to 84 Å), which should lead to greater impregnation of nanoparticles. TEM imaging revealed that calcination of materials for significantly longer than this resulted in a collapse of the material.

Both materials resulting from the assemblage of preformed iron oxide nanoparticles onto support materials were examined by TEM (Fig. 1). In the TEM image of Fe-MCM (Fig. 1a) highlights both the porous structure of the silicate and some nanoparticles across the surface; however, in the case of Fe-puralox (Fig. 1b) the nanoparticles cannot be differentiated from the small alumina crystals of the

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